# 3-*tert*-Butyldimethylsilyloxymethyl-2-lithio-2-phenylsulfonyloxirane as a Glycidyl Anion Equivalent; Preparation of Terminal Epoxy Ketones

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3-*tert*-Butyldimethylsilyloxymethyl-2-phenylsulfonyloxirane **2** is efficiently substituted at the 2-position by deprotonation followed by quenching with electrophiles to give 2-substituted 2-phenylsulfonyloxiranes **4**. These adducts may be converted in a three-step process into epoxy ketones **1** by ring-opening with magnesium bromide to give the α-bromo ketones **9**, desilylation with boron trifluoride–diethyl ether to give the bromohydrins **11** and ring-closure with triethylamine to give the epoxy ketones **1**. Alternatively, treatment of the α-bromo ketones **9** with tetrabutylammonium fluoride gives the epoxy ketones **1** in a single step. The ring-opening reaction with magnesium bromide and the ring-closure reaction with tetrabutylammonium fluoride may be carried out in a one-pot process. 2-Acylated 2-phenylsulfonyloxiranes are able act as acyl transfer agents both in an inter- and an intramolecular sense.

The traditional route to terminal epoxy ketones **1** involves nucleophilic epoxidation of unsaturated ketones with *tert*-butyl hydroperoxide and Triton B,[1] although other nucleophilic epoxidaton systems have also been used.[2] In addition, terminal epoxy ketones have also been prepared by other routes, including ring-closure of α-silyloxy-β-chloro ketones[3] and oxidation of internal alkynes.[4] The Darzens reaction,[5] however, does not appear to have been applied to the synthesis of terminal epoxy ketones, presumably on account of the difficulties associated with the use of formaldehyde. Finally, it should be noted that oxidation of allylic alcohols, or epoxy alcohols, with dimethyldioxirane is a mild method for the preparation of terminal epoxy ketones.[6]

We have recently described synthetic applications of 3-*tert*-butyldimethylsilyloxymethyl-2-phenylsulfonyloxirane **2** as a useful 3-carbon reagent.[7] Deprotonation with butyllithium at low temperature allowed the formation of the lithiated oxirane **3**, which reacted efficiently with a wide range of electrophiles to give the products of substitution **4**. In this paper, we describe our studies aimed at the transformation of these adducts into the terminal epoxy ketones **1**, with a view to demonstrating the synthetic equivalence of the lithiated oxirane **3** to the glycidyl anion **5**. There appear to be no reported examples of synthetic equivalents for this synthon in the literature, although there are several examples of synthetic equivalents for the α,β-unsaturated acyl anion **6**,[8] such as the lithiated allenic ether **7**.[9]

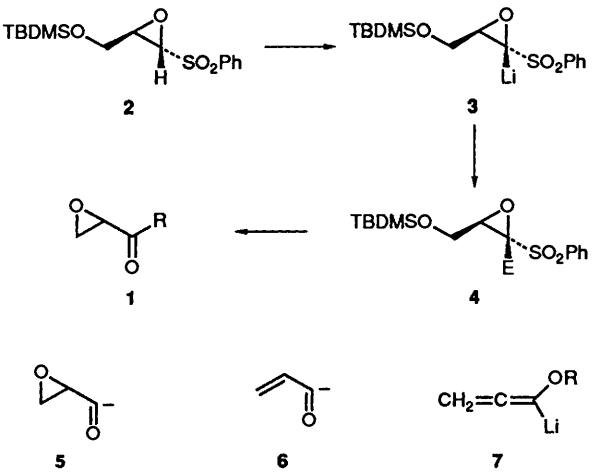
Our initial studies with lithiated phenylsulfonyloxiranes suggested that these species were very unstable and reactive,[7] and we therefore conducted electrophilic substitutions at low temperatures (typically −95 °C in the case of the oxirane **3**). Reaction of lithiated **3** with alkyl halides also required the use of hexamethylphosphoric triamide (HMPA) as a co-solvent. We have subsequently discovered that carcinogenic HMPA can be effectively replaced by 1,3-dimethyl-3,4,5,6-tetrahydro-2(1H)-pyrimidone (DMPU), and that reactions of lithiated **3** can be conducted at −78 °C with no significant loss in yield. These two observations significantly enhance the value of the reagent. Our results for the preparation of new substituted oxiranes **4** are summarised in Table 1. Of some interest was the isolation of the enol acetate **8** from the reaction of lithiated **3** with acetyl chloride.

**Table 1** Reaction of the oxirane **3** with electrophiles

| Electrophile | Product | E | Yield (%) |
|---|---|---|---|
| $C_6H_{13}I$ | **4a** | $C_6H_{13}$ | 80 |
| $C_6H_{13}Br$ | **4a** | $C_6H_{13}$ | 79 |
| $C_5H_{11}I$ | **4b** | $C_5H_{11}$ | 98 |
| $C_5H_{11}Br$ | **4b** | $C_5H_{11}$ | 66 |
| $Ph(CH_2)_2I$ | **4c** | $Ph(CH_2)_3$ | 79 |
| $THPO(CH_2)_6I$ | **4d** | $THPO(CH_2)_6$ | 77 |
| $(CH_2)_5CO$ | **4e** | $(CH_2)_5C(OH)$ | 98 |
| $(CH_2)_4CO$ | **4f** | $(CH_2)_4C(OH)$ | 98 |
| $Ph(CH_2)_2CHO$ | **4g** | $Ph(CH_2)_2CH(OH)$ | 81[a] |
| PhCHO | **4h** | PhCH(OH) | 83[b] |
| $CH_2{=}CHCH_2Br$ | **4i** | $CH_2{=}CHCH_2$ | 91 |
| $PhCH{=}CHCH_2Br$ | **4j** | $PhCH{=}CHCH_2$ | 93 |
| PhCOCl | **4k** | PhCO | 68 |
| MeCOCl | **4l** | MeCO | 36[c] |
| $MeCO_2Me$ | **4l** | MeCO | 61 |
| Bu$^t$COCl | **4m** | Bu$^t$CO | 76 |
| 4-$MeOC_6H_4COCl$ | **4n** | 4-$MeOC_6H_4CO$ | 67 |

[a] Chromatographically separable 45:36 mixture of diastereoisomers. [b] Chromatographically separable 52:31 mixture of diastereoisomers. [c] The enol acetate **8** was also isolated (20%).

Reaction of the oxiranes **4** with magnesium bromide–diethyl



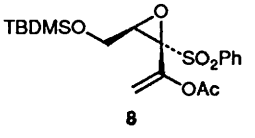



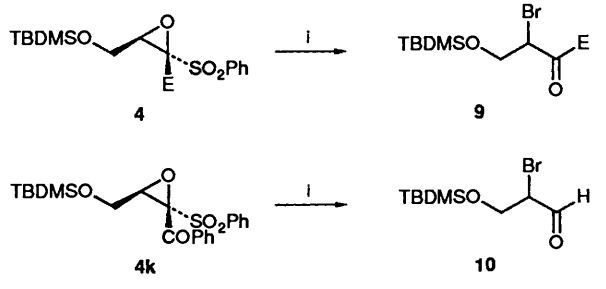
**Table 2** Reaction of the oxiranes **3** and **4** with $MgBr_2$

| Oxirane | E | Product | Yield (%) |
|---|---|---|---|
| **3** | H | **10** | 100 |
| **4a** | $C_6H_{13}$ | **9a** | 92 |
| **4c** | $Ph(CH_2)_3$ | **9c** | 78 |
| **4d** | $THPO(CH_2)_6$ | **9d** | 63 |
| **4e** | $(CH_2)_5C(OH)$ | **9e** | 70 |
| **4f** | $(CH_2)_4C(OH)$ | **9f** | 100 |
| **4i** | $CH_2{=}CHCH_2$ | **9i** | 72 |
| **4j** | $PhCH{=}CHCH_2$ | **9j** | 96 |
| **4k** | PhCO | **10** | 97 |

**Table 3** Preparation of the epoxy ketones **1** by deprotection of the silyl ethers **9**, and ring-closure of the bromohydrins **11**

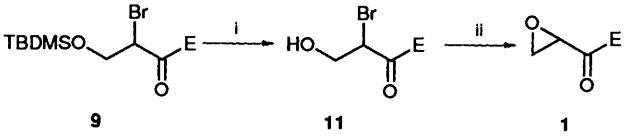
| Silyl ether | E | Bromohydrin | Yield (%) | Epoxy ketone | Yield (%) |
|---|---|---|---|---|---|
| **9a** | $C_6H_{13}$ | **11a** | 91 | **1a** | 63 |
| **9c** | $Ph(CH_2)_3$ | **11c** | 97 | **1c** | 87 |
| **9d** | $THPO(CH_2)_6$ | **11d** | 0 | **1d** | — |
| **9e** | $(CH_2)_5C(OH)$ | **11e** | 68 | **1e** | 7 |

ether[10] occurred uneventfully to give the α-bromo ketones **9** in good yield (Table 2). However, reaction of the 2-benzoyl derivative **4k** gave the glyceraldehyde derivative **10**, rather than the expected product (Scheme 1). Presumably, deacylation is effected by bromide attack at the carbonyl group, in the reverse of the reaction by which the compound was formed. This reaction precludes the preparation of epoxy diketones such as **1k** by this approach. The glyceraldehyde derivative **10** could also be prepared directly by treatment of **2** with $MgBr_2$, and represents a useful method for the preparation of this highly functionalised aldehyde.



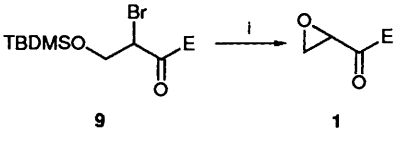

**Scheme 1** *Reagents and conditions:* i, $MgBr_2$·$Et_2O$, $Et_2O$, room temp.

Conversion of the silyl ethers **9** into the corresponding bromohydrins **11** was achieved by the use of boron trifluoride–diethyl ether.[11] This reagent proved to be especially useful for this purpose (*vide infra*). The simple unfunctionalised bromohydrins **11** could be converted in good yield into the epoxy ketones **1** by treatment with triethylamine in dichloromethane (Scheme 2, Table 3).* It was of interest that the bromohydrin **11o** (E = $PhCH_2$) which we had previously prepared decomposed completely under these conditions, and indeed under all other conditions that we investigated for the cyclisation of the bromohydrins II. The epoxy ketone **1o** has been postulated as an intermediate in the reaction of a closely related phenylsulfinyloxirane with pyridinium toluene-*p*-sulfonate and propan-1-ol.[13]




**Scheme 2** *Reagents and conditions:* i, $BF_3$·$Et_2O$, $CH_2Cl_2$, room temp.; ii, $Et_3N$, $CH_2Cl_2$, room temp.

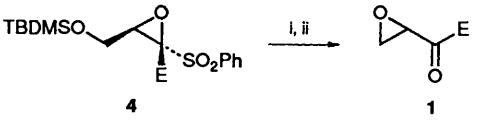
Whilst the process was efficient for simple bromohydrins, it was significantly less effective for functionalised examples such as **11e**. We therefore examined the direct conversion of the silyl ethers **9** into the epoxy ketones **1** using reagents which would be expected to generate an alkoxide intermediate which could then cyclise to the epoxy ketone. Indeed, treatment of the silyl ethers **9** with either caesium fluoride in acetonitrile or tetrabutylammonium fluoride (TBAF) in tetrahydrofuran gave the desired epoxy ketones directly in one step (Table 4, Scheme 3). The




**Scheme 3** *Reagents and conditions:* $Bu_4NF$, 1 mol $dm^{-3}$ in THF, r.t.

use of TBAF gave higher yields and the reactions were generally more convenient to perform.† The reaction failed completely for the substrates **9i**, **9j** and **9o**, which all possess particularly acidic protons adjacent to the carbonyl group. It is of interest that ring-closure of the corresponding bromohydrins **11** could also be effected with TBAF, although the reaction was significantly slower.

In a final effort to improve the scope and convenience of the process, we have investigated the possibility of carrying out the conversion of the sulfonyl oxiranes **4** into the epoxy ketones **1** in a one-pot reaction. Reaction of the sulfonyl oxiranes **4** with $MgBr_2$ in diethyl ether was carried out as previously described, and TBAF was added when TLC indicated that all the sulfonyl oxirane had been consumed. Purification of the epoxy ketones was generally carried out by direct chromatography on silica gel, which avoided significant losses of the more water-soluble epoxy ketones during work-up. This one-pot process allows the preparation of a range of functionalised epoxy ketones in moderate to good overall yield (Table 5, Scheme 4).




**Scheme 4** *Reagents and conditions:* i, $MgBr_2$·$Et_2O$, $Et_2O$, room temp.; ii, $Bu_4NF$, 1 mol $dm^{-3}$ in THF, room temp.

In view of the ready deacylation of the oxirane **4k** by $MgBr_2$, we decided to establish whether other reagents could effect this process. Treatment of the silyl ether **4k** with boron trifluoride–diethyl ether gave the alcohol **12k** (which existed as a mixture with the two epimeric lactols) in good yield, again confirming that this is the reagent of choice for desilylation of the silyl ethers

* Triethylamine has been used previously for the preparation of epoxy ketones from α-bromo-β-hydroxy ketones, prepared by tin(II) triflate-mediated aldol reaction of terminal α-bromo ketones with aldehydes.[12]

† This is in contrast to the results of Hünig (ref. 3) who found that ring-closure of α-silyloxy-β-chloro ketones with TBAF gave significantly lower yields than the corresponding reactions employing either CsF or KF.

**Table 4** Preparation of the epoxy ketones **1** by treatment of the silyl ethers **9** with fluoride

| Silyl ether | E | Reagent | Product | Yield (%) |
|---|---|---|---|---|
| **9c** | $Ph(CH_2)_3$ | TBAF | **1c** | 42 |
| **9d** | $THPO(CH_2)_6$ | TBAF | **1d** | 49 |
| **9f** | $(CH_2)_4C(OH)$ | TBAF | **1f** | 19 |
| **9f** | $(CH_2)_4C(OH)$ | CsF | **1f** | 11 |

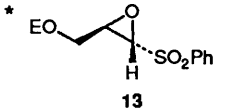
**Table 5** Preparation of the epoxy ketones **1** by treatment of the oxiranes **4** with $MgBr_2$, followed by TBAF in a one-pot process

| Oxirane | E | Epoxy ketone | Yield (%) |
|---|---|---|---|
| **4a** | $C_6H_{13}$ | **1a** | 62 |
| **4b** | $C_5H_{11}$ | **1b**[a] | 76 |
| **4c** | $Ph(CH_2)_3$ | **1c** | 63 |
| **4d** | $THPO(CH_2)_6$ | **1d** | 35 |
| **4e** | $(CH_2)_5C(OH)$ | **1e** | 39 |
| **4f** | $(CH_2)_4C(OH)$ | **1f** | 35 |

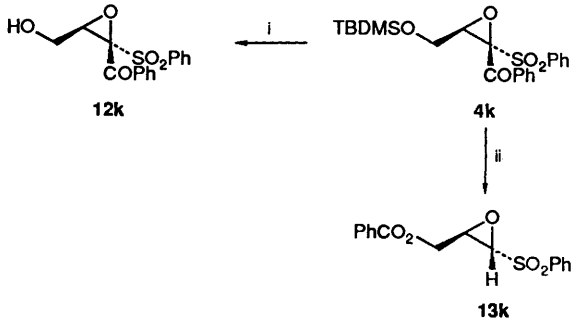
[a] This compound has been described in the literature,[17] but without spectroscopic details.

**Table 6** Acyl transfer reactions of 2-acyl-2-phenylsulfonyloxiranes

| Oxirane | E | Product* | Yield (%) |
|---|---|---|---|
| **4k** | PhCO | 13k | 63 |
| **4l** | MeCO | 13l | 41 |
| **4m** | Bu$^t$CO | 13m | 78 |
| **4n** | 4-$MeOC_6H_4CO$ | 13n | 82 |




**13**




**Scheme 5** *Reagents and conditions:* i, $BF_3$·$Et_2O$, $CH_2Cl_2$, room temp.; ii, $Bu_4NF$, 1 mol $dm^{-3}$ in THF, room temp.

**4** without side-reactions. However, treatment of **4k** with TBAF gave the benzoyloxy derivative **13k** (Scheme 5). This compound presumably arises as a result of a 1,4 C to O acyl migration. Other acylated sulfonyl oxiranes also undergo this 1,4-acyl migration (Table 6). Such 1,4 acyl transfer reactions are well-documented in the sense O to C,[14,15] although there appears only to be a single prior example of a rearrangement from C to O.[16] The position of equilibrium in our examples must reflect some release of steric compression, as well as the significant anion-stabilising ability of the phenylsulfonyloxirane group. Both these factors must also be important in the ability of acylated sulfonyl oxirane to act as acyl transfer reagents with nucleophiles such as bromide (*vide supra*).

## Experimental

For general experimental procedures see ref. 7. All NMR spectra were recorded in $CDCl_3$ as solvent. *J* Values are given in Hz. In listing of mass spectra, peaks due to $^{79}Br$ only are recorded. Light petroleum refers to that fraction with boiling point 40–60 °C, unless otherwise stated. Tetrabutylammonium fluoride was obtained from Aldrich as a 1 mol $dm^{-3}$ solution in tetrahydrofuran.

*General Procedure for the Reactions of* trans-3-tert-*Butyldimethylsilyloxymethyl-2-phenylsulfonyloxirane* **2**.—A solution of *trans-3-tert*-butyldimethylsilyloxymethyl-2-phenylsulfonyloxirane **2** in dry THF (10 $cm^3$ per mmol) was cooled to −100 °C. Butyllithium (1.1 equiv.) was added at below −95 °C and the mixture then stirred at −95 °C for 10 min. A solution of the electrophile in dry THF (0.5 $cm^3$) was then added. The reaction mixture was warmed to the temperature indicated, aqueous $NH_4Cl$ (10% solution; 5 $cm^3$) was added and the reaction mixture was allowed to warm to room temp. The mixture was extracted into ethyl acetate (3 × 10 $cm^3$), and the combined organic extracts were dried and evaporated. The residue was then purified by flash chromatography using 10:1 light petroleum–ethyl acetate unless stated otherwise. Reactions can be conveniently conducted on scales up to 10 mmol.

trans-3-tert-*Butyldimethylsilyloxymethyl-2-hexyl-2-phenylsulfonyloxirane* **4a**. The electrophile, iodohexane (2 equiv.) was added as a solution in DMPU (2 equiv.) and THF and the reaction mixture was warmed to −75 °C over 25 min. The oxirane **4a** (77%) was a colourless oil (Found: C, 61.1; H, 8.9. $C_{21}H_{36}O_4SSi$ requires C, 61.1; H, 8.8%); $\nu_{max}$(film)/$cm^{-1}$ 2957, 2930, 2859, 1449, 1327, 1258, 1152 and 839; $\delta_H$(200 MHz) 0.06 (3 H, s), 0.07 (3 H, s), 0.84 (3 H, t, *J* 6.2), 0.88 (9 H, s), 1.19–1.25 (6 H, m), 1.49–1.94 (4 H, m), 3.68–3.87 (3 H, m), 7.53–7.73 (3 H, m) and 7.90–7.95 (2 H, m); *m/z* (EI) 413 ($MH^+$, 2%), 355 (15), 325 (35), 271 (55), 125 (82) and 85 (100).

Alternatively, addition of hexyl bromide (2 equiv.), as a solution in DMPU (2 equiv.) and THF, to the lithiated oxirane **3**, followed by stirring for 23 h at −78 °C, gave the oxirane **4a** (79%) after work-up.

trans-3-tert-*Butyldimethylsilyloxymethyl-2-pentyl-2-phenylsulfonyloxirane* **4b**. The electrophile, iodopentane (2 equiv.) was added as a solution in DMPU (2 equiv.) and THF and the reaction mixture was warmed to −80 °C over 15 min. The residue was purified by flash chromatography using 15:1 light petroleum–ethyl acetate as eluent, to yield the oxirane **4b** (77%), as a colourless oil (Found: C, 60.1; H, 8.75. $C_{20}H_{34}O_4SSi$ requires C, 60.3, H, 8.75%); $\nu_{max}$(film)/$cm^{-1}$ 3050, 2957, 2930, 2858, 1472, 1464, 1327, 1258, 1152 and 816; $\delta_H$(200 MHz) 0.06 (3 H, s), 0.07 (3 H, s), 0.82 (3 H, t, *J* 6.6), 0.88 (9 H, s), 1.16–1.26 (5 H, m), 1.58–1.89 (3 H, m), 3.71–3.87 (3 H, m), 7.53–7.74 (3 H, m) and 7.90–7.96 (2 H, M); *m/z* (EI) 399 ($MH^+$, 1%), 369 (0.4), 353 (0.4), 341 (2), 311 (5), 241 (3), 215 (4), 125 (54) and 99 (100).

Alternatively, addition of pentyl bromide (2 equiv.), as a solution in DMPU (2 equiv.) and THF, to the lithiated oxirane **3**, followed by stirring for 23 h at −78 °C, gave the oxirane **4b** (66%) after work-up.

trans-3-tert-*Butyldimethylsilyloxymethyl*-2-(3-*phenylpropyl*)-2-*phenylsulfonyloxirane* **4c**. The electrophile, 3-phenylpropyl iodide (2 equiv.), was added as a solution in DMPU (2 equiv.) and THF and the reaction mixture was warmed to −80 °C over 5 min and then stirred at −80 °C for 15 min before being quenched. The oxirane **4c** (79%) was a colourless oil (Found: C, 64.9; H, 7.8. $C_{24}H_{34}O_4SSi$ requires C, 64.5; H, 7.7%); $\nu_{max}$(film)/$cm^{-1}$ 2955, 2858, 1325, 1257, 1151 and 839; $\delta_H$(300 MHz) 0.03 (3 H, s), 0.05 (3 H, s), 0.88 (9 H, s), 1.55–1.70 (1 H, m), 1.73–1.82 (2 H, m), 1.84–2.07 (1 H, m), 2.54 (2 H, t, *J* 7.1), 3.59–3.81 (3 H, m), 7.07–7.10 (2 H, m), 7.17–7.29 (3 H, m), 7.49–7.54 (2 H,

m), 7.65–7.69 (1 H, m) and 7.79–7.82 (2 H, m); *m/z* 373 ($M^+ - C_4H_9$, $CH_3$, 4%), 3.59 (4), 247 (25), 199 (39), 125 (62) and 91 (100).

trans-3-tert-*Butyldimethylsilyloxymethyl*-2-*phenylsulfonyl*-2-[6-(*tetrahydropyran*-2-*yloxy*)*hexyl*]*oxirane* **4d**. The electrophile, 6-(tetrahydropyran-2-yloxy)hexyl iodide (2 equiv.), was added as a solution in DMPU (2 equiv.) and THF and the reaction mixture was warmed to −80 °C over 15 min. The oxirane **4d** (77%) was a colourless oil; $\nu_{max}$(film)/cm$^{-1}$ 2936, 2859, 1260, 1152 and 1084; $\delta_H$(200 MHz) 0.04 (3 H, s), 0.06 (3 H, s), 0.88 (9 H, s), 1.1–1.25 (6 H, m), 1.4–1.86 (10 H, m), 3.27–3.39 (1 H, m), 3.46–3.54 (1 H, m), 3.63–3.90 (5 H, m), 4.55 (1 H, m, br), 7.53–7.73 (3 H, m) and 7.89–7.94 (2 H, m); *m/z* (EI) 455 ($M^+ - C_4H_9$, 0.5%), 425 (1), 341 (2), 125 (44) and 85 (100).

trans-3-tert-*Butyldimethylsilyloxymethyl*-2-(1-*hydroxycyclohexyl*)-2-*phenylsulfonyloxirane* **4e**. The electrophile was cyclohexanone (2 equiv.) and the reaction mixture was warmed to −80 °C over 15 min and stirred at −80 °C for 20 min. The oxirane **4e** (98%) was a pale yellow oil which was used without purification. A sample solidifed with time, m.p. 81–83 °C (Found: C, 58.8; H, 8.1. $C_{21}H_{34}O_5SSi$ requires C, 59.1; H, 8.0%); $\nu_{max}$(film)/cm$^{-1}$ 3539, 2957, 2930, 2897, 2856, 1476, 1464, 1451, 1321, 1154 and 1097; $\delta_H$(300 MHz) 0.3 (3 H, s), 0.4 (3 H, s), 0.9 (9 H, s), 1.2–1.4 (1 H, m), 1.49–1.72 (7 H, m), 1.95 (OH, s, br), 2.01–2.11 (2 H, m), ABX system ($\delta_A$ 4.03, $\delta_B$ 4.08, $\delta_X$ 3.55, $J_{AB}$ 12.8, $J_{AX}$ 5.4, $J_{BX}$ 3.4), 7.51–7.68 (3 H, m) and 7.91–7.95 (2 H, m); *m/z* (EI) 409 ($M^+$ − OH, 7), 379 (5), 351 (11), 339 (12), 125 (80), 75 (100) and 99 (88).

trans-3-tert-*Butyldimethylsilyloxymethyl*-2-(1-*hydroxycyclopentyl*)-2-*phenylsulfonyloxirane* **4f**. The electrophile was cyclopentanone (2 equiv.) and the reaction mixture was warmed to −50 °C over 15 min. The residue was purified by flash chromatography using 15:1 light petroleum–ethyl acetate as eluent to yield the oxirane **4f** (90%), as a pale yellow oil, a sample of which eventually solidified, m.p. 49–51 °C (Found: C, 58.2; H, 8.3. $C_{20}H_{32}O_5SSi$ requires C, 58.2; H, 7.8%); $\nu_{max}$(film)/cm$^{-1}$ 3480, 3067, 2957, 2878, 1305, 1148 and 590; $\delta_H$(200 MHz) 0.04 (6 H, s), 0.85 (9 H, s), 1.49–1.95 (8 H, m), 2.64 (1 H, br), ABX system ($\delta_A$ 3.88, $\delta_B$ 4.03, $\delta_X$ 3.67, $J_{AB}$ 12.7, $J_{AX}$ 5.6, $J_{BX}$ 3.1), 7.50–7.71 (3 H, m) and 7.90–7.95 (2 H, m); *m/z* (EI) 413 ($MH^+$, 1%), 395 (10), 271 (10), 125 (85) and 85 (100).

trans-2-(1-*Hydroxy*-3-*phenylpropyl*)-3-tert-*butyldimethylsilyloxy*-2-*phenylsulfonyloxirane* **4g**. *trans*-3-*tert*-Butyldimethylsilyl-2-phenylsulfonyloxirane **2** was lithiated at −78 °C. The electrophile was 3-phenylpropanal (2 equiv.) and the reaction mixture was stirred at −78 °C for 3 h. The two diastereoisomeric oxiranes **4g** were obtained after chromatography. The oxirane with higher $R_f$ was a solid (45%), m.p. 76–78 °C (Found: C, 62.4; H, 7.3. $C_{24}H_{34}O_5SSi$ requires C, 62.3; H, 7.4%); $\nu_{max}$(KBr)/cm$^{-1}$ 3430, 2957, 2936, 2924, 2957, 1325, 1157 and 1059; $\delta_H$(500 MHz) 0.08 (6 H, s), 0.89 (9 H, s), 1.81–1.88 (1 H, m), 2.38–2.68 (1 H, m), 2.77–2.98 (3 H, m), 3.87 (1 H, d, br, *J* 9.8), ABX system ($\delta_A$ 3.99, $\delta_B$ 4.06, $\delta_X$ 3.99, $J_{AB}$ 12.4, $J_{AX}$ 5.7, $J_{BX}$ 3.4), 7.12–7.34 (7 H, m), 7.46–7.49 (1 H, m) and 7.62–7.67 (2 H, m); *m/z* (EI) 463 ($MH^+$, 25%), 445 (20), 321 (50), 217 (70), 117 (100), 105 (85), 91 (85) and 77 (90).

The oxirane with lower $R_f$ was a solid (36%), m.p. 51–54 °C (Found: C, 62.8; H, 7.4. $C_{24}H_{34}O_5SSi$ requires C, 62.3; H, 7.4%); $\nu_{max}$(KBr)/cm$^{-1}$ 3494, 3065, 3027, 2957, 2930, 2857, 1308, 1148 and 839; $\delta_H$(500 MHz) 0.06 (3 H, s), 0.07 (3 H, s), 0.88 (9 H, s), 1.53–1.60 (1 H, m), 1.99–2.04 (1 H, m), 2.51–2.57 (1 H, m), 2.65–2.70 (1 H, m), 2.82 (1 H, d, *J* 6.8), ABX system ($\delta_A$ 3.75, $\delta_B$ 3.93, $\delta_X$ 3.8, $J_{AB}$ 12.4, $J_{AX}$ 5.5, $J_{BX}$ 3.6), 4.11–4.17 (1 H, m), 7.03–7.06 (2 H, m), 7.09–7.30 (3 H, m), 7.50–7.53 (2 H, m), 7.64–7.68 (1 H, m) and 7.82–7.84 (2 H, m); *m/z* (EI) 463 ($MH^+$, 50%), 446 (55), 216 (50), 142 (100), 117 (90), 91 (64) and 75 (62).

trans-3-tert-*Butyldimethylsilyl*-2-(1-*hydroxybenzyl*)-2-*phenylsulfonyloxirane* **4h**. The electrophile was benzaldehyde (2 equiv.) and the reaction mixture was warmed to −40 °C over 30 min. The residue was purified by flash chromatography using 15:1 light petroleum–ethyl acetate as eluent to yield two diastereoisomeric oxiranes **4h**. The oxirane with higher $R_f$ was a solid (52%), m.p. 62–64 °C (Found: C, 61.2; H, 6.9) $C_{22}H_{30}O_5SSi$ requires C, 60.8; H, 7.0%); $\nu_{max}$(KBr)/cm$^{-1}$ 3488, 3063, 2955, 2930, 2886, 2857, 1321, 1150 and 839; $\delta_H$(500 MHz) 0.10 (3 H, s), 0.11 (3 H, s), 0.91 (9 H, s), 3.81 (1 H, br s), 3.87 (1 H, dd, *J* 12.5, 5.9), 4.15 (1 H, dd, *J* 12.5, 3.4), 4.23 (1 H, dd, *J* 5.9, 3.4), 5.01 (1 H, s, br) and 7.07–7.47 (10 H, m); *m/z* (EI) 417 ($M^+$ − OH, 1%), 3.77 (1), 361 (1), 125 (75) and 75 (100).

The oxirane with lower $R_f$ was an oil (31%) (Found: C, 60.9; H, 7.1. $C_{22}H_{30}O_5SSi$ requires C, 60.8; H, 7.0%); $\nu_{max}$(film)/cm$^{-1}$ 3509, 3065, 3032, 2955, 2930, 2886, 2857, 1310, 1088 and 837; $\delta_H$(500 MHz) −0.10 (3 H, s), −0.07 (3 H, s), 0.81 (9 H, s), 3.45 (1 H, dd, *J* 12.5, 6.5), 3.66 (1 H, s, br), 3.77 (1 H, dd, *J* 12.5, 3.9), 3.95 (1 H, dd, *J* 6.5, 3.9), 5.58 (1 H, s, br), 7.05–7.09 (2 H, m), 7.18–7.25 (3 H, m), 7.53–7.57 (2 H, m), 7.67–7.71 (1 H, m) and 7.88–7.90 (2 H, m); *m/z* (EI) 417 ($M^+$ − OH, 25%), 359 (12), 329 (5), 125 (70) and 43 (100).

trans-2-*Allyl*-3-tert-*butyldimethylsilyloxymethyl*-2-*phenylsulfonyloxirane* **4i**. The electrophile, allyl bromide (2 equiv.), was added as a solution in DMPU (2 equiv.) and THF and the reaction mixture was warmed to −80 °C over 15 min. The residue was purified by flash chromatography using 15:1 light petroleum–ethyl acetate as eluent to yield the oxirane **4i** (86%), as a colourless oil (Found: C, 58.6; H, 7.9. $C_{18}H_{28}O_4SSi$ requires C, 58.7; H, 7.7%); $\nu_{max}$(film)/cm$^{-1}$ 2955, 2930, 2886, 2859, 1472, 1327, 1152, 1088 and 839; $\delta_H$(200 MHz) 0.06 (3 H, s), 0.07 (3 H, s), 0.88 (9 H, s), AB part of an ABXYZ system ($\delta_A$ 2.55, $\delta_B$ 2.69, $J_{AB}$ 16.3, $J_{AX}$ 6.6, $J_{AY}$ 1.5, $J_{AZ}$ 1.4, $J_{BX}$ 7.1, $J_{BY}$ 1.4, $J_{BZ}$ 1.4), 3.67–3.88 (3 H, m), 4.97–5.08 (2 H, m), 5.58–5.78 (1 H, m), 7.46–7.67 (3 H, m) and 7.83–7.88 (2 H, m); *m/z* (EI) 369 ($MH^+$, 0.1%), 311 (4), 281 (12), 125 (73) and 73 (100).

trans-3-tert-*Butyldimethylsilyloxymethyl*-2-(3-*phenylprop*-2-*enyl*)-2-*phenylsulfonyloxirane* **4j**. The electrophile, 3-phenylprop-2-enyl bromide (2 equiv.), was added as a solution in DMPU (2 equiv.) and THF and the reaction mixture was warmed to −80 °C and stirred at that temperature for 15 min. The residue was purified by flash chromatography using 15:1 light petroleum–ethyl acetate as eluent to yield the oxirane **4j** (93%), as a colourless oil (Found: $M^+ - C_4H_9$, 387.1169. $C_{20}H_{23}O_4SSi$ requires 387.1087); $\nu_{max}$(film)/cm$^{-1}$ 3061, 3027, 2955, 2930, 2886, 2859, 1391, 1325, 1310, 1150, 1117, 839 and 723; $\delta_H$(200 MHz) 0.06 (3 H, s), 0.08 (3 H, s), 0.88 (9 H, s), 2.87 (2 H, m), 3.81–3.98 (3 H, m), 5.93 (1 H, dt, *J* 15.9, 7.0), 6.32 (1 H, m), 7.15–7.32 (5 H, m), 7.45–7.64 (3 H, m) and 7.89–7.94 (2 H, m); *m/z* (EI) 414 ($M^+ - 2CH_3$, 2%), 387 ($M^+ - C_4H_9$, 11), 357 (7) and 117 (100).

trans-2-*Benzoyl*-3-tert-*butyldimethylsilyloxymethyl*-2-*phenylsulfonyloxirane* **4k**. The electrophile was benzoyl chloride (2 equiv.) and the reaction mixture was warmed to −80 °C over 10 min. The residue was recrystallised from light petroleum (b.p. 60–80 °C)–ethyl acetate to give the oxirane **4k** (68%), as a white solid, m.p. 73–75 °C (Found: C, 60.9; H, 6.4. $C_{22}H_{28}O_5SSi$ requires C, 61.1; H, 6.5%); $\nu_{max}$(KBr)/cm$^{-1}$ 2930, 2859, 1682, 1323, 1154 and 839; $\delta_H$(200 MHz) −0.25 (3 H, s), −0.21 (3 H, s), 0.66 (9 H, s), AB part of an ABX system ($\delta_A$ 3.73, $\delta_B$ 4.04, $J_{AB}$ 12.9, $J_{AX}$ 3.1, $J_{BX}$ 2.8), 4.18 (1 H, m), 7.37–7.71 (6 H, m), 7.75–7.81 (2 H, m) and 7.91–7.99 (2 H, m); *m/z* (FAB) 433 ($MH^+$, 4%), 375 (3), 345 (1), 319 (1), 301 (11), 205 (20), 125 (15), 105 (100) and 73 (41).

*Reaction between* trans-3-tert-*butyldimethylsilyloxymethyl*-2-*phenylsulfonyloxirane* **3** *and acetyl chloride*. The electrophile was acetyl chloride (2.1 equiv.) and the reaction mixture was warmed to −80 °C over 10 min and stirred at the same temperature for 10 min. The residue was purified using 20:1 toluene–ethyl acetate as the eluent to yield two oxiranes: trans-2-(1′-*acetoxyvinyl*)-3-tert-*butyldimethylsilyloxymethyl*-2-*phenylsulf*-

*onyloxirane* **8** with a higher $R_f$ (20%), was a white solid, m.p. 68–71 °C 55.3; H, 6.9. $C_{19}H_{28}O_6SSi$ requires C, 55.3; H, 6.8%); $\nu_{max}$(film)/cm$^{-1}$ 3060, 2950, 2930, 2890, 2860, 1780, 1320, 1160 and 837; $\delta_H$(200 MHz) 0.04 (3 H, s), 0.05 (3 H, s), 0.87 (9 H, s), 2.11 (3 H, s), ABX system ($\delta_A$ 3.60, $\delta_B$ 4.01, $\delta_X$ 4.11, $J_{AB}$ 12.1, $J_{AX}$ 6.9, $J_{BX}$ 3.5), 4.98 (1 H, d, *J* 2.2), 5.12 (1 H, d, *J* 2.2), 7.49–7.71 (3 H, m) and 7.86–7.92 (2 H, m); *m/z* (FAB) 413 ($MH^+$, 15%), 355 (18), 229 (50), 125 (36) and 73 (100); and trans-2-*acetyl*-3-tert-*butyldimethylsilyloxymethyl*-2-*phenylsulfonyloxirane* **4** with a lower $R_f$ (36%) was a white solid, m.p. 82–83 °C (from light petroleum–ethyl acetate) (Found: C, 55.6; H, 7.0. $C_{17}H_{26}O_5SSi$ requires C, 55.1; H, 7.1%); $\nu_{max}$(Nujol)/cm$^{-1}$ 3036, 3015, 2860, 1720, 1315, 1155 and 835; $\delta_H$(200 MHz) 0.00 (3 H, s), 0.01 (3 H, s), 0.83 (9 H, s), 2.25 (3 H, s), 3.86–4.13 (3 H, m), 7.54–7.62 (2 H, m), 7.68–7.76 (1 H, m) and 7.84–7.89 (2 H, m); *m/z* (EI) 371 ($MH^+$, 2%), 271 (52), 229 (23), 199 (15), 177 (50), 143 (42) and 125 (100).

trans-2-*Acetyl*-3-tert-*butyldimethylsilyloxymethyl*-2-*phenylsulfonyloxirane* **4l**. The electrophile was methyl acetate (2 equiv.) and the reaction mixture was warmed to −80 °C over 10 min and stirred at the same temperature for 10 min. The residue was recrystallised from light petroleum–ethyl acetate to yield the oxirane **4l** (61%) as a white solid.

trans-3-tert-*Butyldimethylsilyloxymethyl*-2-*phenylsulfonyl*-2-*trimethylacetyloxirane* **4m**. *trans*-3-*tert*-Butyldimethylsilyl-2-phenylsulfonyloxirane **2** was lithiated at −78 °C. The electrophile was pivaloyl chloride (2 equiv.) and the reaction mixture was stirred for 20 min. The oxirane **4m** (76%) was a colourless oil (Found: C, 58.3; H, 7.85. $C_{20}H_{32}O_5SSi$ requires C, 58.2; H, 7.8%); $\delta_H$(200 MHz)–0.03 (3 H, s), 0.01 (3 H, s), 0.83 (9 H, s), 1.26 (9 H, s), ABX system ($\delta_A$ 3.41, $\delta_B$ 3.73, $\delta_X$ 3.58, $J_{AB}$ 12.2, $J_{AX}$ 6.1, $J_{BX}$ 3.1), 7.54–7.76 (3 H, m) and 7.83–7.88 (2 H, m); $\nu_{max}$(film)/cm$^{-1}$ 3069, 2959, 2932, 2885, 2859, 1705, 1331, 1157 and 838; *m/z* (EI) (367 (2%), 325 (2), 271 (46), 125 (83), 75 (83 and 57 (100).

trans-3-tert-*Butyldimethylsilyloxymethyl*-2-(4-*methoxybenzoyl*)-2-*phenylsulfonyloxirane* **4n**. *trans*-3-*tert*-Butyldimethylsilyl-2-phenylsulfonyloxirane **2** was lithiated at −78 °C. The electrophile was 4-methoxybenzoyl chloride (2 equiv.) and the reaction mixture was stirred at −78 °C for 20 min. The oxirane **4n** (67%) was a colourless oil (Found: C, 60.3; H, 6.7. $C_{23}H_{30}O_6SSi$ requires C, 59.7, H, 6.5%); $\nu_{max}$(film)/cm$^{-1}$ 2955, 2930, 2899, 2589, 1676, 1601, 1329, 1157 and 837; $\delta_H$(200 MHz) 0.2 (3 H, s), −0.16 (3 H, s), 0.71 (9 H, s), ABX system ($\delta_A$ 3.70, $\delta_B$ 3.92, $\delta_X$ 4.15, $J_{AB}$ 12.8, $J_{AX}$ 3.9, $J_{BX}$ 3.0), 3.87 (3 H, s), 6.86–6.90 (2 H, m), 7.47–7.54 (2 H, m), 7.62–7.70 (1 H, m), 7.76–7.80 (2 H, m) and 7.88–7.94 (2 H, m); *m/z* (EI) 406 ($MH^+ - C_4H_9$, 20%), 375 (51), 135 (100) and 77 (46).

*General Procedure for the Reactions between the Oxiranes* **2** *and* **4** *and Magnesium Bromide–Diethyl Ether*.—Solid magnesium bromide–diethyl ether (1.3 equiv., unless stated otherwise) was added to a 0.1 mol dm$^{-3}$ solution of the oxirane in dry diethyl ether. The mixture was stirred at room temp. (3–5 h) until all the oxirane had been consumed. The mixture was diluted with light petroleum (20 cm$^3$ per mmol) and filtered through a Celite pad. The Celite was washed with further petroleum (2 × 30 cm$^3$) and the combined filtrates were concentrated. The residue was purified by flash chromatography using the eluent indicated to yield the α-bromo carbonyl derivatives.

2-*Bromo*-3-tert-*butyldimethylsilyloxypropanal* **10**. Solid magnesium bromide–diethyl ether (1.2 equiv.) was added to the oxirane **2**. The filtrate was concentrated to yield the bromo aldehyde **10** as a colourless oil (100%) (Found: C, 40.4; H, 7.5. $C_9H_{19}BrO_2Si$ requires C, 40.45; H, 7.2%); $\nu_{max}$(film)/cm$^{-1}$ 2957, 2932, 2886, 2859, 1732, 839 and 779; $\delta_H$(200 MHz) 0.06 (6 H, s), 0.86 (9 H, s), 3.95–4.06 (2 H, m), 4.16–4.22 (1 H, m) and 9.49 (1 H, d, *J* 3.4); *m/z* (EI) 267 ($MH^+$, 2%), 209 (20), 181 (100), 139 (65), 129 (85) and 101 (80).

2-*Bromo*-3-tert-*butyldimethylsilyloxypropanal* **10**. The residue from reaction of oxirane **4k** was purified by flash chromatography using 10:1 light petroleum–ethyl acetate as eluent to yield the bromo aldehyde **10** as a colourless oil (97%).

2-*Bromo*-1-tert-*butyldimethylsilyloxynonan*-3-*one* **9a**. Solid magnesium bromide–diethyl ether (1.6 equiv.) was added to the oxirane **4a**. The combined filtrates were concentrated to yield the bromo ketone **9a** as a colourless oil (92%) (Found: $M^+$, 350.1297. $C_{15}H_{31}BrO_2Si$ requires 350.1277); $\nu_{max}$(film)/cm$^{-1}$ 2957, 2930, 2859, 1723, 1472, 1464, 1258 and 839; $\delta_H$(200 MHz) 0.06 (3 H, s), 0.07 (3 H, s), 0.75–0.91 (3 H, m), 0.86 (9 H, s), 1.20–1.30 (6 H, m), 1.50–1.64 (2 H, m) and 2.66 (2 H, t, *J* 7.3), ABX system ($\delta_A$ 3.89, $\delta_X$ 4.06, $\delta_B$ 4.25, $J_{ab}$ 5.4, $J_{AX}$ 10.3, $J_{BX}$ 8.3); *m/z* (EI) 351 ($MH^+$, 10%), 295 (73), 265 (45), 213 (45) and 43 (100).

2-*Bromo*-1-tert-*butyldimethylsilyl*-6-*phenylhexan*-3-*one* **9c**. Reaction with the oxirane **4c** was carried out using dry THF as the solvent. The residue was purified by flash chromatography using 20:1 light petroleum (b.p. 60–80 °C)–ethyl acetate as eluent to yield the bromo ketone **9c** as a colourless oil (78%) (Found: $M^+ - CH_3$, 369.0824. $C_{17}H_{26}BrO_2Si$ requires 369.0886); $\alpha_{max}$(film)/cm$^{-1}$ 2955, 2930, 2886, 2859, 1720, 1472, 1462, 1362 and 839; $\delta_H$(300 MHz) 0.05 (3 H, s), 0.06 (3 H, s), 0.86 (9 H, s), 1.96 (2 H, dt, *J* 15.0, 7.5), 2.63–2.73 (4 H, m), ABX system ($\delta_A$ 3.89, $\delta_X$ 3.89, $\delta_X$ 4.05, $\delta_B$ 4.24, $J_{AB}$ 10.4, $J_{AX}$ 5.5, $J_{BX}$ 5.4), 7.17–7.21 (3 H, m) and 7.28–7.29 (2 H, m); *m/z* (EI) 385 ($MH^+$, <1%), 369 (1), 329 (1), 247 (27), 105 (52), 91 (100), 155 (55) and 129 (55).

1-(2-*Bromo*-3-tert-*butyldimethylsilyloxypropionyl*)*cyclohexanol* **9e**. From the oxirane **4e**, the bromo ketone **9e** was obtained as a colourless oil (70%) (Found: $MH^+$, 365.1167. $C_{15}H_{30}BrO_3Si$ requires 365.1148); $\nu_{max}$(film)/cm$^{-1}$ 3449, 2932, 2883, 2857, 1713 and 839; $\delta_H$(200 MHz) 0.03 (3 H, s), 0.07 (3 H, s), 0.85 (9 H, s), 1.05–1.28 (1 H, m), 1.45–1.80 (9 H, m) and 3.06 (1 H, s, br), ABX system ($\delta_A$ 3.86, $\delta_B$ 4.91, $\delta_X$ 4.08, $J_{AB}$ 9.7, $J_{AX}$ 5.2, $J_{BX}$ 5.3); *m/z* (EI) 309 ($MH^+ - {}^tBu$, 15%), 291 (20), 217 (20), 99 (84), 81 (81) and 75 (100).

1-(2-*Bromo*-3-tert-*butyldimethylsilyloxypropionyl*)*cyclopentanol* **9f**. From the oxirane **4f**, the bromo ketone **9f** was obtained as a colourless oil (100%) (Found: C, 48.5; H, 8.0. $C_{14}H_{27}BrO_3Si$ requires C, 47.9; H, 7.75%); $\nu_{max}$(film)/cm$^{-1}$ 3507, 2957, 2932, 2884, 2859, 1717, 1258, 1101 and 839; $\delta_H$(300 MHz) 0.04 (3 H, s), 0.07 (3 H, s), 0.86 (9 H, s), 1.64–1.70 (1 H, m), 1.74–1.82 (3 H, m), 1.89–1.97 (2 H, m), 2.10–2.22 (2 H, m), 3.34 (1 H, s, br), 3.89 (1 H, dd, *J* 9.7, 5.1), 4.13 (1 H, t, *J* 9.7) and 4.71 (1 H, dd, *J* 9.7, 5.1); *m/z* (EI) 351 ($MH^+$, 16), 33 (35), 293 (32), 277 (42), 275 (26), 247 (26), 213 (50), 67 (54) and 55 (100).

2-*Bromo*-1-tert-*butyldimethylsilyloxyhex*-5-*en*-3-*one* **9i**. Solid magnesium bromide–diethyl ether (1.0 equiv.) was added to the oxirane **4i**. The solvent was removed under reduced pressure and the residue was purified by flash chromatography using 5:1 light petroleum (b.p. 60–80 °C)–ethyl acetate to yield the bromo ketone **9i** as a colourless oil (72%) (Found: C, 47.3; H, 7.8. $C_{12}H_{23}BrO_2Si$ requires C, 46.9; H, 7.5%); $\nu_{max}$(film)/cm$^{-1}$ 3085, 2957, 2930, 2886, 2859, 1726, 1258, 1100 and 839; $\delta_H$(500 MHz) 0.06 (3 H, s), 0.07 (3 H, s), 0.87 (9 H, s), AB part of an ABX system ($\delta_A$ 3.42, $\delta_B$ 3.47, $J_{AB}$ 17.4, $J_{AX}$ 6.7, $J_{BX}$ 6.9), 3.91 (1 H, dd, *J* 10.6, 5.4), 4.07 (1 H, dd, *J* 10.6, 8.2), 4.32 (1 H, dd, *J* 8.2, 5.4), 5.18 (1 H, dq, *J* 17.2, 1.2, 1.2), 5.23 (1 H, dq, *J* 10.2, 1.2, 1.2) and 5.88–5.69 (1 H, m); *m/z* (EI) 307 ($MH^+$, 4%), 265 (8), 250 (95), 169 (100) and 139 (90).

2-*Bromo*-1-tert-*butyldimethylsilyloxy*-6-*phenylhex*-5-*en*-3-*one* **9j**. Solid magnesium bromide–diethyl ether (1.6 equiv.) was added to the oxirane **4j**. The residue was purified by flash chromatography using 10:1 light petroleum (b.p. 60–80 °C)–ethyl acetate as eluent to yield the bromo ketone **9j** as a colourless oil (96%) (Found: $M^+$, 382.1928. $C_{18}H_{27}BrO_2Si$

requires 382.0964); $\nu_{max}$(film)/cm$^{-1}$ 2955, 2930, 2886, 2859, 1725, 1101 and 839; $\delta_H$(200 MHz) 0.07 (3 H, s), 0.08 (3 H, s), 0.87 (9 H, s), 3.57–3.63 (2 H, m), ABX system ($\delta_A$ 3.65, $\delta_B$ 4.52, $\delta_X$ 4.10, $J_{AB}$ 10.5, $J_{AX}$ 4.6, $J_{BX}$ 5.5), 6.30 (1 H, dt, *J* 15.9, 6.7), 6.51 (1 H, m) and 7.19–7.41 (5 H, m); *m/z* (EI) 382 ($M^+$, 1%), 326 (1), 245 (50), 117 (83) and 74 (100).

*General Procedure for the Reaction of Sylyl Ethers* **9** *with Boron Trifluoride–Diethyl Ether.*—Boron trifluoride–diethyl ether (1.5 equiv.) was added to a 0.1 mol dm$^{-3}$ solution of the silyl ether **9** in dry dichloromethane (10 cm$^3$) at room temp. The mixture was stirred at room temp. for 2.5 h, diluted with dichloromethane (10 cm$^3$), and washed with aqueous sodium carbonate (10 cm$^3$). The aqueous layer was extracted with dichloromethane (10 cm$^3$) and the combined organic extracts were dried and concentrated to give the bromo alcohol **11**.

2-*Bromo*-1-*hydroxynonan*-3-*one* **11a**. The silyl ether **9a** gave the bromo alcohol **11a** as an oil (91%) (Found: $M^+$, 236.0477. $C_9H_{17}BrO_2$ requires 236.0412); $\nu_{max}$(film)/cm$^{-1}$ 3409, 2957, 2930, 2859, 1713, 1462 and 1379; $\delta_H$(200 MHz) 0.85–0.99 (3 H, m), 1.25–1.39 (6 H, m), 1.55–1.69 (2 H, m), 2.21 (1 H, br s), AB part of an $ABX_2$ system ($\delta_A$ 2.60, $\delta_B$ 2.84, $J_{AB}$ 17.3, $J_{AX}$ 7.1, $J_{BX}$ 7.5), ABX system ($\delta_A$ 3.92, $\delta_B$ 4.03, $\delta_X$ 4.37 $J_{AB}$ 12.1, $J_{AX}$ 7.5, $J_{BX}$ 7.4); *m/z* (EI) 237 ($MH^+$, 71%), 219 (47), 157 (46), 113 (96) and 85 (100).

2-*Bromo*-1-*hydroxy*-6-*phenylhexan*-3-*one* **11c**. The silyl ether **9c** gave the bromo alcohol **11c** as an oil (97%) (Found: C, 53.3; H, 5.55. $C_{12}H_{15}BrO_2$ requires C, 53.3; H, 5.6%); $\nu_{max}$(film)/cm$^{-1}$ 3428, 3059, 3029, 2938, 1713, 1265 and 739; $\delta_H$(200 MHz) 1.97 (2 H, m), 2.30 (1 H, s, br), 2.59 (1 H, dt, *J* 17.8, 7.2), 2.60–2.69 (2 H, m), 2.90 (1 H, dt, *J* 17.8, 7.2), ABX system ($\delta_A$ 3.89, $\delta_B$ 4.03, $\delta_X$ 4.33, $J_{AB}$ 12.1, $J_{AX}$ 5.1, $J_{BX}$ 4.3), 7.15–7.34 (5 H, m); *m/z* (EI) 271 ($MH^+$, 1%), 254 (10), 191 (37), 173 (66), 104 (100) and 91 (90).

1-(2-*Bromo*-3-*hydroxypropionyl*)*cyclohexanol* **11e**. Using the silyl ether **9e**, the combined organic extracts were dried and concentrated to give a residue. Purification by flash chromatography using light petroleum (b.p. 60–80 °C)–ethyl acetate 5:1 as eluent gave the bromo alcohol **11e** (68%) which solidified with time, m.p. 64–66 °C (Found: C, 43.0; H, 6.0. $C_9H_{15}BrO_3$ requires C, 43.05; H, 6.0%); $\nu_{max}$(film)/cm$^{-1}$ 3387, 1709 and 1049; $\delta_H$(200 MHz) 1.05–1.40 (1 H, m), 1.63–1.89 (9 H, m), 3.39 (2 H, s, br), ABX system ($\delta_A$ 3.85, $\delta_B$ 4.00, $\delta_X$ 4.96, $J_{AB}$ 11.6, $J_{AX}$ 8.4, $J_{BX}$ 5.4); *m/z* (EI) 251 ($MH^+$, 37%), 233 (63%), 215 (54), 153 (58), 99 (95) and 81 (100).

*General Procedure for the Ring-closure Reactions of Bromohydrins* **11** *using Triethylamine.*—Triethylamine (5 equiv.) was added to a 0.05–0.08. mol dm$^{-3}$ solution of the bromohydrin **11** in dry dichloromethane (5 cm$^3$). The mixture was stirred at room temp. for the time indicated. Phosphate buffer (pH 7, 1 mol dm$^{-3}$; 10 cm$^3$) was added and the mixture was extracted with dichloromethane (3 × 10 cm$^3$). The organic extracts were combined, washed with brine (10 cm$^3$), dried ($Na_2SO_4$) and concentrated. The residue was purified by flash chromatography using 5:1 light petroleum (b.p. 60–80 °C)–ethyl acetate as eluent, unless otherwise stated, to give the epoxy ketone **1**.

1,2-*Epoxynonan*-3-*one* **1a**. Using the bromohydrin **11a**, the mixture was stirred at room temp. overnight and the solvent was removed under reduced pressure. The residue was purified by flash chromatography using 10:1 light petroleum (b.p. 60–80 °C)–ethyl acetate as eluent to give the epoxy ketone **1a** as a pale yellow oil (63%) (Found: C, 69.2; H, 10.7. $C_9H_{16}O_2$ requires C, 69.2; H, 10.3%); $\nu_{max}$(film)/cm$^{-1}$ 2932, 2858, 1716, 1468, 1379, 1278, 1234 and 871; $\delta_H$(200 MHz) 0.84–0.91 (3 H, m), 1.16–1.41 (6 H, m), 1.50–1.64 (2 H, m), AB part of an $ABX_2$ system ($\delta_A$ 2.19, $\delta_B$ 2.33, $J_{AB}$ 17.2, $J_{AX}$ 7.3, $J_{BX}$ 7.4), 2.85 (1 H, dd, *J* 5.9, 2.5), 2.98 (1 H, dd, *J* 5.9, 4.6) and 3.42 (1 H, dd, *J* 4.6, 2.5); *m/z* (EI) 157 ($MH^+$, 28%), 113 (85) (76) and 42 (100).

1,2-*Epoxy*-6-*phenylhexan*-3-*one* **1c**. Using the bromohydrin **11c**, the mixture was stirred at room temp. for 24 h and diluted with dichloromethane (15 cm$^3$). The epoxy ketone **1c** was a colourless oil (87%) (Found: C, 75.7; H, 7.4. $C_{12}H_{14}O_2$ requires C, 75.8; H, 7.4%); $\nu_{max}$(film)/cm$^{-1}$ 3085, 3063, 3027, 2930, 2861, 1713, 1455, 750 and 700; $\delta_H$(200 MHz) 1.92 (2 H, m), AB part of an $ABX_2$ system ($\delta_A$ 2.30, $\delta_B$ 2.45, $J_{AB}$ 17.6, $J_{AX}$ 7.2, $J_{BX}$ 7.4), 2.62 (2 H, t, *J* 7.5), 2.80 (1 H, dd, *J* 5.8, 2.5), 2.96 (1 H, dd, *J* 5.8, 4.7), 3.41 (1 H, dd, *J* 4.7, 2.5) and 7.14–7.33 (5 H, m); *m/z* (EI) 190 ($M^+$, 3%), 172 (43), 159 (54), 147 (50), 130 (60), 117 (63), 104 (100) and 91 (90).

1-(2,3-*Epoxypropionyl*)*cyclohexanol* **1e**. Using the bromohydrin **11e**, the mixture was stirred at room temp. for 72 h. The epoxy ketone **1e** was a colourless oil (7%) (Found: $M^+$, 170.0914; $C_9H_{14}O_3$ requires 170.0911); $\nu_{max}$(film)/cm$^{-1}$ 3464, 3065, 2936, 2860, 1718, 1377 and 1098; $\delta_H$(200 MHz) 1.22–1.29 (2 H, m), 1.61–1.83 (8 H, m), 2.85 (1 H, dd, *J* 6.7, 2.5), 3.02 (1 H, dd, *J* 6.7, 4.5), 3.09 (1 H, br s) and 3.96 (1 H, dd, *J* 4.5, 2.5); *m/z* (EI) 170 ($M^+$ 0.1%), 153 (10), 99 (95), 81 (100), 55 (75) and 43 (83).

1,2-*Epoxy*-6-*phenylhexan*-3-*one* **1c**. Tetrabutylammonium fluoride trihydrate (0.425 g, 1.348 mmol) was added to a solution of the silyl ether **9c** (0.165 g, 0.428 mmol) in dry THF (1.8 cm$^3$) and the mixture was stirred for 15 min. Phosphate buffer (pH 7, 1 mol dm$^{-3}$; 5 cm$^3$) was added and the mixture extracted with dichloromethane (3 × 10 cm$^3$) The dried ($Na_2SO_4$) extracts were then concentrated and the residue was purified by flash chromatography using 20:1 light petroleum (b.p. 60–80 °C)–ethyl acetate as eluent to give the epoxy ketone **1c** as a colourless oil (0.034 g, 42%).

1,2-*Epoxy*-9-(*tetrahydropyran*-2-*yloxy*)*nonan*-3-*one* **1d**. Tetrabutylammonium fluoride trihydrate (0.240 g, 0.760 mmol) was added to a solution of the silyl ether **9d** (0.10 g, 0.222 mmol) in dry THF (1.5 cm$^3$) and the mixture was stirred for 5 min. Phosphate buffer (pH 7, 1 mol dm$^{-3}$; 5 cm$^3$) was added to the mixture which was then extracted with ethyl acetate (3 × 10 cm$^3$). The dried ($Na_2SO_4$) extracts were concentrated and the residue was purified by flash chromatography using 2:1 light petroleum (b.p. 60–80 °C)-ethyl acetate as eluent to give the epoxy ketone **1d** as a colourless oil (0.028 g, 49%) (Found: C, 65.8; H, 9.8. $C_{14}H_{24}O_4$ requires C, 65.6; H, 9.4%); $\nu_{max}$(film)/cm$^{-1}$ 3059, 2940, 2865, 1713, 1261 and 1033; $\delta_H$(200 MHz) 1.24–1.90 (14 H, m), AB part of an $ABX_2$ system ($\delta_A$ 2.27, $\delta_B$ 2.41, $J_{AB}$ 17.3, $J_{AX}$ 7.3, $J_{BX}$ 7.4), 2.85 (1 H, dd, *J* 5.8, 2.5), 2.98 (1 H, dd, *J* 5.8, 4.7), 3.30–3.54 (2 H, m), 3.42 (1 H, dd, *J* 4.7, 2.5), 3.66–3.77 (1 H, m), 3.80–3.91 (1 H, m) and 4.55 (1 H, m); *m/z* (EI), 256 ($M^+$, 2%), 213 (3), 173 (35), 155 (34) and 85 (100).

1-(2,3-*Epoxypropionyl*)*cyclopentanol* **1f**. Tetrabutylammonium fluoride (1 mol dm$^{-3}$ solution in THF; 0.86 cm$^3$, 0.86 mmol) was added to a solution of the silyl ether **9f** (0.101 g, 0.288 mmol) in dry THF (2.0 cm$^3$) and the mixture was stirred for 1 h. The solvent was removed from the mixture under reduced pressure. The residue was purified by flash chromatography using 5:1 light petroleum (b.p. 60–80 °C)–ethyl acetate as eluent to give the epoxy ketone **1f** as a colourless oil (0.0085 g, 19%) (Found: $MH^+$, 157.0874. $C_8H_{13}O_3$ requires 157.0891); $\nu_{max}$(film)/cm$^{-1}$ 3453, 2961, 2874 and 1717; $\delta_H$(200 MHz) 1.69–2.20 (8 H, m), 2.92 (1 H, dd, *J* 6.7, 2.5), 3.04 (1 H, dd, *J* 6.7, 4.4), 3.42 (1 H, s) and 3.75 (1 H, dd, *J* 4.4, 2.5); *m/z* (EI) 157 ($MH^+$, 4%), 139 (15), 85 (100), 67 (93), 41 (94) and 29 (68).

1-(2,3-*Epoxypropionyl*)*cyclopentanol* **1f**. Caesium fluoride (0.080 g, 0.529 mmol) as a suspension in dry acetonitrile (2 cm$^3$) was added to a solution of the silyl ether **9f** (0.124 g, 0.352 mmol) in dry acetonitrile (2 cm$^3$) at 0 °C. The mixture was allowed to warm to room temp. and then stirred overnight. The mixture was filtered through a silica pad and the filtrate was concentrated. The residue was purified by flash chromato-

graphy using 5:1 light petroleum (b.p. 60–80 °C)–ethyl acetate as eluent to give the epoxy ketone **1f** as a colourless oil (0.006 g, 11%).

*General Procedure for the One-pot Ring-closure Reactions of the Oxiranes* **4**.—Solid magnesium bromide–diethyl ether (1.6 equiv.) was added to a solution of the oxirane **4** (5 mmol) in dry diethyl ether (50 $cm^3$) and the mixture was stirred at room temp. until all the oxirane **4** had been consumed. Dry THF (10 $cm^3$) was added to the mixture, followed by TBAF (1 mol $dm^{-3}$ solution in THF; 3 equiv.). The reaction was followed by TLC until all the intermediate **9** was consumed. The mixture was filtered through Celite. The Celite was washed with diethyl ether (2 × 100 $cm^3$) and dichloromethane (3 × 20 $cm^3$), unless otherwise indicated, and the filtrates were combined and concentrated. The residue was purified by flash chromatography using 5:1 light petroleum (b.p. 30–40 °C)–diethyl ether as eluent, unless otherwise indicated, to yield the epoxy ketone **1**.

1,2-*Epoxynonan*-3-*one* **1a**. The oxirane **4a** gave the epoxy ketone **1a** in 62% yield.

1,2-*Epoxyoctan*-3-*one* **1b**. Using the oxirane **4b**, the solution was filtered through a Celite pad, which was washed with dichloromethane (50 $cm^3$). The filtrates were combined and concentrated and the epoxy ketone **1b** was obtained in 76% yield (Found: C, 67.5; H, 10.1. $C_8H_{14}O_2$ requires C, 67.6; H, 9.9%); $\nu_{max}$(film)/$cm^{-1}$ 2959, 2934, 2874, 2863, 1715, 1468, 1379, 1235 and 870; $\delta_H$(200 MHz) 0.84–0.96 (3 H, m), 1.10–1.41 (4 H, m), 2.19–2.31 (2 H, m), AB part of an $ABX_2$ system ($\delta_A$ 2.22, $\delta_B$ 2.31, $J_{AB}$ 17.0, $J_{AX}$ 7.3, $J_{BX}$ 7.4), 2.85 (1 H, dd, *J* 5.9, 2.5), 2.98 (1 H, dd, *J* 5.9, 4.6) and 3.42 (1 H, dd, *J* 4.6, 2.5); *m*/*z* (EI) 142 ($M^+$, 0.3%), 113 (1), 99 (78), 86 (51), 71 (77), 55 (47) and 43 (100).

1,2-*Epoxy*-6-*phenylhexan*-3-*one* **1c**. Using the oxirane **4c**, the Celite was washed with diethyl ether (2 × 50 $cm^3$) and dichloromethane (2 × 50 $cm^3$) and the filtrates were combined and concentrated. The residue was purified by flash chromatography using 10:1 light petroleum (b.p. 30–40 °C)–diethyl ether as eluent to yield the epoxy ketone **1c** (63%).

1,2-*Epoxy*-9-(*tetrahydropyran*-2-*yloxy*)*nonan*-3-*one* **1d**. Using the oxirane **4d**, the solution was filtered through Celite and washed with diethyl ether (50 $cm^3$) and ethyl acetate (50 $cm^3$) and the filtrates were combined and concentrated. The residue was purified by flash chromatography using 5:1 light petroleum–ethyl acetate as eluent to yield the epoxy ketone **1d** (35%).

1-(2,3-*Epoxypropanionyl*)*cyclohexanol* **1e**. Using the oxirane **4e**, the mixture was passed through a short silica pad and concentrated. The residue was purified by flash chromatography using 5:1 light petroleum–ethyl acetate as eluent to give the epoxy ketone **1e** (39%).

1-(2,3-*Epoxypropionyl*)*cyclopentanol* **1f**. Using the oxirane **4e**, the solution was filtered through a silica pad and the filtrate was concentrated to give the epoxy ketone **1f** in 35%.

2-*Benzoyl*-3-*hydroxymethyl*-2-*phenylsulfonyloxirane* **12**.—The oxirane **4k** (0.433 g, 1.0 mmol), was dissolved in dichloromethane (10 $cm^3$) and boron trifluoride–diethyl ether (0.19 $cm^3$, 1.55 mmol) was added. The mixture was stirred at room temp. until all **4k** had been consumed (48 h). The solvent was removed under reduced pressure and the residue was purified by flash chromatography using light petroleum–ethyl acetate 2:1 as eluent to give the oxirane **12** as a foam (0.323 g, 100%) (Found: C, 60.5; H, 4.55. $C_{16}H_{14}O_5S$ requires C, 60.4; H, 4.4%); $\nu_{max}$(film)/$cm^{-1}$ 3515, 3065, 2930, 1682, 1329 and 1157; $\delta_H$(200 MHz) 2.81 (1 H, s, br), 3.23–4.24 (m) and 4.53 (s), (total 3 H) and 7.06–7.95 (10 H, m); *m*/*z* (EI) 301 ($M^+ - OH$, 30%), 177 (28), 125 (28), 105 (100) and 77 (66).

*General Procedure for the Reactions of the Oxiranes* **4** *with Tetrabutylammonium Fluoride*.—Tetrabutylammonium fluoride (1 mol $dm^{-3}$ solution in THF; 3 equiv.) was added to a 0.1 mol $dm^{-3}$ solution of the oxirane **4** in dry THF (5 $cm^3$). The mixture was stirred at room temp. until TLC indicated that all **4** had been consumed. The solvent was removed under reduced pressure and the residue was purified by flash chromatography using light petroleum–ethyl acetate 5:1 as eluent to yield the oxirane **13**. The oxiranes were recrystallised from ethyl acetate–light petroleum.

trans-3-*Benzoyloxymethyl*-2-*phenylsulfonyloxirane* **13k**. The oxirane **4k** gave the oxirane **13k** (63%), m.p. 96–98 °C (Found: C, 60.5; H, 4.1. $C_{16}H_{14}O_5S$ requires C, 60.4; H, 4.4%); $\nu_{max}$(film)/$cm^{-1}$ 3065, 2961, 1725, 1449, 1329, 1271, 1179 and 1088; $\delta_H$(200 MHz) 4.05 (1 H, ddd, *J* 4.8, 2.8, 1.7), 4.21 (1 H, d, *J* 1.7), AB part of an ABX system ($\delta_A$ 4.36, $\delta_B$ 4.78, $J_{AB}$ 13.0, $J_{AX}$ 4.8, $J_{BX}$ 2.8), 7.39–7.47 (2 H, m), 7.53–7.76 (4 H, m) and 7.92–8.03 (4 H, m); *m*/*z* (EI) 319 ($MH^+$, 0.3%), 177 (80), 125 (55), 105 (100) and 77 (95).

trans-3-*Acetoxymethyl*-2-*phenylsulfonyloxirane* **13l**. The oxirane **4l** gave the oxirane **13l** (41%), m.p. 71–72 °C (Found: C, 51.4; H, 4.7. $C_{11}H_{12}O_5S$ requires C, 51.55; H, 4.7%); $\nu_{max}$(KBr)/$cm^{-1}$ 3073, 3009, 2955, 1738, 1327, 1157 and 750; $\delta_H$(200 MHz) 2.05 (3 H, s), 3.89 (1 H, ddd, *J* 4.6, 2.7, 1.6), 4.11 (1 H, dd, *J* 13.0, 4.6), 4.13 (1 H, d, *J* 1.6), 4.50 (1 H, dd, *J* 13.0, 2.7), 7.55–7.76 (3 H, m), 7.90–7.96 (2 H, m); *m*/*z* (EI) 257 ($MH^+$ 43%), 197 (41), 141 (42), 125 (74), 115 (100) and 77 (53).

trans-3-*Trimethylacetoxymethyl*-2-*phenylsulfonyloxirane* **13m**. The oxirane **4m** gave the oxirane **13m** (78%), m.p. 86–87 °C (Found: C, 56.0; H, 6.0. $C_{14}H_{18}O_5S$ requires C, 56.4; H, 6.1%); $\nu_{max}$(KBr)/$cm^{-1}$ 3067, 3045, 3025, 2978, 1740, 1316, 1146 and 748; $\delta_H$(200 MHz) 1.18 (9 H, s), 3.80 (1 H, ddd, *J* 4.7, 2.8, 1.7), 4.10 (1 H, dd, *J* 12.9, 4.7), 4.10 (1 H, d, *J* 1.7), 4.50 (1 H, dd, *J* 12.9, 2.8), 7.57–7.87 (3 H, m) and 7.92–7.97 (2 H, m); *m*/*z* (EI) 299 ($MH^+$, 7%), 157 (91), 141 (23), 125 (95), 109 (38), 85 (68), 77 (78) and 57 (100).

trans-3-(4-*Methoxybenzoyloxymethyl*)-2-*phenylsulfonyloxirane* **13n**. The oxirane **4n** gave the oxirane **13n** (82%), m.p. 86–88 °C (Found: C, 58.5; H, 4.65. $C_{17}H_{16}O_6S$ requires C, 58.6; H, 4.6%); $\nu_{max}$(KBr)/$cm^{-1}$ 3003, 2957, 1701, 1159 and 855; $\delta_H$(200 MHz) 3.86 (3 H, s), 4.02 (1 H, ddd, *J* 4.7, 2.8, 1.7), 4.19 (1 H, d, *J* 1.7), 4.35 (1 H, dd, *J* 13.0, 4.7), 4.73 (1 H, dd, *J* 13.0, 2.8), 6.91 (2 H, m), 7.56–7.76 (3 H, m) and 7.95 (4 H, m); *m*/*z* (EI) 348 ($M^+$, 5%), 207 (42), 152 (43), 135 (100), 125 (36), 107 (15), 92 (28) and 77 (58).

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